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Palladium/Carbon Dioxide Cooperative Catalysis for the Production of Diketone Derivatives from Carbohydrates

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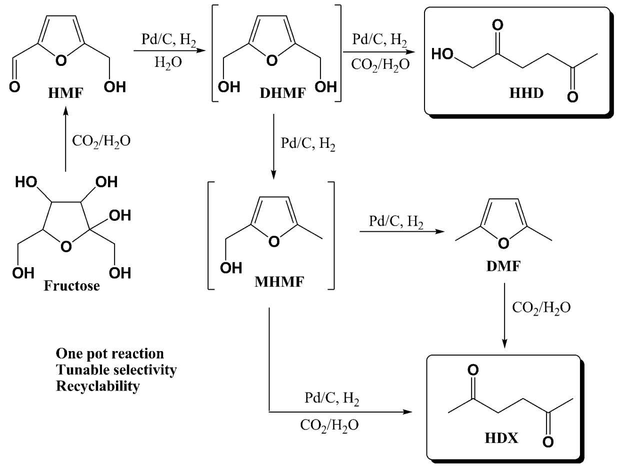
The one-pot production of industrially valuable diketone derivatives from carbohydrates is achieved through a bifunctional catalytic process. In particular, Pd/C-catalyzed hydrogenation of HMF in water and under CO_2 affords 1-hydroxypentane-2,5-dione with up to 77 % yield. The process is also eligible starting from fructose and inulin, affording 1-hydroxyhexane-2,5-dione with 36 % and 15 % yield, respectively. The key of the process is reversible in situ formation of carbonic acid, which is capable of assisting Pd/C during the hydrogenation reaction by promoting the dehydration of carbohydrates and the ring-opening of furanic intermediates. Interestingly, by changing the reaction medium from H_2O to a H_2O/THF mixture (1:9), it is possible to switch the selectivity of the reaction and to produce 2,5-hexanadione with 83 % yield. Within the framework of sustainable chemistry, reactions presented in this report show 100 % carbon economy, involve CO_2 to generate acidity, require water as a solvent, and are conducted under rather low hydrogen pressures (10 bar).

Several decades ago, the rational design of bifunctional catalysts emerged as a smart concept to maximize the eco-efficiency of chemical processes.[1] This concept, initially developed for the conversion of fossil chemicals, has since been applied to carbohydrates in order to produce fine chemicals or fuels.[2] In this context, the association of acid and redox active sites in a single catalyst or reactor has clearly emerged as an effective way to create chemical diversity from carbohydrates with a minimal number of reaction steps. The deposition of transition metals over an acid solid support is the most commonly adopted strategy.[2] Although promising results have been reported recently, the presence of water as a contaminant of carbohydrates or as an inescapable solvent for their dissolution often led to irreversible deactivation of the acid support, and this aspect is nowadays the topic of intense research. To date, the search for innovative and selective routes capable of converting carbohydrates to valuable fine chemicals in a single reactor is of huge industrial interest.

Carbon dioxide (CO_2) is known to readily react with water to form carbonic acid. Herein, we show that Pd/C-catalyzed hydrogenation of carbohydrates or furanic derivatives in a CO_2/H_2O system is a promising strategy to produce, in a unique reactor, diketone derivatives through a dual acid-/redox-catalytic process. Diketone derivatives are an interesting class of chemicals, especially for the production of diols or diamines, which have strong market potential in the field of polymers (polyethers, polyamides, polyesters), solvents, and surfactants. In addition, diketone derivatives are also used to produce valuable pharmaceutical ingredients, such as pyrrolidine as recently highlighted by Turner.[3] Diketone derivatives are currently produced from fossil resources, and industrial demand for bio-based routes is high.

The main molecules (and their abbreviations) described in this work are illustrated in Scheme 1. Among the valuable structures generated herein, we emphasize the production of the 1-hydroxyhexane-2,5-dione (HHD) derivative that was obtained from 5-hydroxymethylfurfural (HMF), fructose, or inulin. To date, the synthesis of HHD has been scarcely reported and we found only two reports dealing with its production, both involving 5-hydroxymethyfurfural (HMF) as a starting material.[4] To the best of our knowledge, there is no report on the direct conversion of carbohydrates into HHD.



Scheme 1. Scientific strategy of this work and abbreviation of main chemicals discussed in this work.

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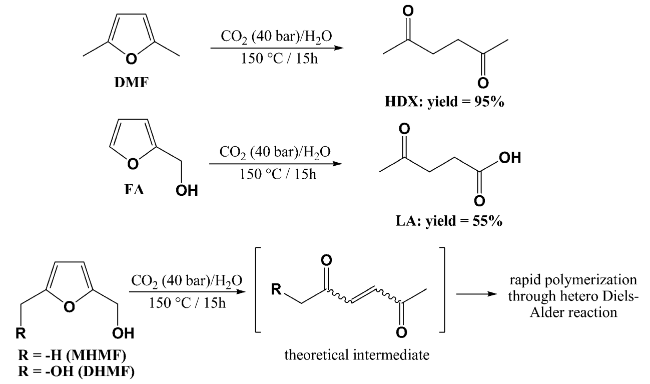
A similar conclusion can be drawn for 2,5-hexanedione (HDX) which is only mentioned as a side product (yield < 10 %) in current literature reports focusing on furanic derivatives. As a general trend, most reported studies focus on catalytic reduction of the C=O or C=C bonds of bio-derived furanic derivatives, and only little attention is given to the catalytic ring-opening (hydrolysis) of intermediate furanic derivatives to diketones.[5]

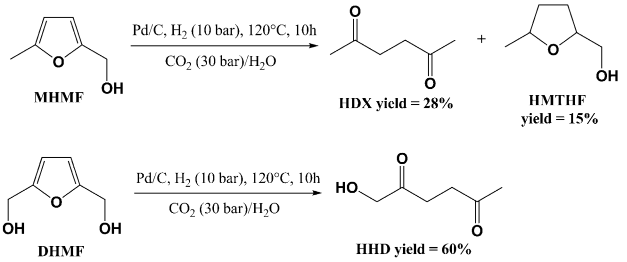
To demonstrate the advantage offered by the CO_2/H_2O system for the production of diketone derivatives from biomass, we first investigated the ring-opening of furanic derivatives that are readily obtained from carbohydrates. In a first set of experiments, dimethylfuran (DMF), a key intermediate of the furanic platform, was used as a substrate. When DMF was heated at 150 °C for 15 h in neat water, no reaction occurred. Conversion of DMF was observed once CO_2 was added, thus confirming the crucial role of CO_2 on the reactivity of DMF. Remarkably, under optimized pressure of CO_2 (40 bar), DMF was completely and selectively hydrolyzed to the corresponding 2,5-hexanedione (HDX) (> 95 % yield) at 150 °C (Scheme 2). After release of the CO_2 pressure (release of H_2O and CO_2), HDX was conveniently isolated in pure form after distillation of water, thus bypassing all traditional steps required to purify the reaction products and to recycle (or reactivate) the acid solid catalyst. Next, we screened other valuable furanic derivatives known to be formed as intermediates from carbohydrates. Furfuryl alcohol (FA), a highly reactive furanic derivative, was also converted (in a route with 100 % carbon economy) in neat water and under CO_2 to levulinic acid with a reaction yield (55 %) in a similar range than those previously claimed in the presence of solid acid catalysts (Scheme 2).[6]



Scheme 2. Catalytic ring-opening of furanic derivatives in the CO_2/H_2O system.

2-methyl-5-hydroxymethylfuran (MHMF) and 2,5-dihydroxymethylfurane (DHMF), both obtained by hydrogenation/hydrogenolysis of 5-hydroxymethylfurfural (HMF), were also fully converted in the CO_2/H_2O system after 15 h of reaction (Scheme 2). However, the selectivity of the reaction was fairly low in these cases. This low selectivity stems from the fact that the acid-catalyzed ring opening of MHMF and DHMF can lead to readily polymerizable derivatives under acidic conditions (Scheme 2).

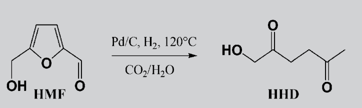
To produce the targeted diketone derivatives from MHMF and DHMF, hydrogen and a metal catalyst were introduced into the reactor for in situ reduction of the intermediate unsaturated diketone. Pd/C is a widely used water-tolerant solid catalyst at an industrial scale, and was thus selected in our study. In a typical experiment, MHMF and DHMF were heated in water at 120 °C for 10 h in the presence of 2 wt % of Pd/C, 10 bar of hydrogen, and 30 bar of CO_2 (Scheme 3). Under these acid/redox conditions, we were pleased to see that it was possible to drive the catalytic reaction to the targeted diketone derivatives. In the case of MHMF, competition occurred between the production of HDX (28 % yield) and the reduction of the furanic ring to 2-methyl-5-hydroxymethyltetrahydrofurane (HMTHF, 15 % yield). Other products were not identified. From DHMF, however, the catalytic reaction was more selective and HHD was obtained with 60 % yield.



Scheme 3. Dual acid/redox catalytic conversion of hydroxymethylfuranic derivatives in the presence of Pd/C, H_2, CO_2, and H_2O.

The CO_2/H_2O system being capable of catalyzing the ring-opening of furanic derivatives, we then investigated the reactivity of HMF in the presence of the CO_2/H_2O system; a more challenging task. When HMF was reacted in the same CO_2/H_2O system for converting DMF and FA as aforementioned, no reaction occurred suggesting that, in these conditions, carbonic acid does not have a sufficient pK_a value to catalyze the ring-opening of HMF. DHMF is the primary product obtained during hydrogenation of HMF. Hence, catalytic conversion of HMF using the dual CO_2/H_2O-Pd/C/H_2 system was investigated with the aim of converting HMF to HHD in a one-pot reaction. To our delight, when HMF was reacted in neat water in the presence of 7.5 wt % of Pd/C and a pressure of H_2 and CO_2 of 10 bar and 30 bar, respectively, HHD was produced with 77 % yield (Table 1, entry 1). In this reaction, it was necessary to find a compromise between the CO_2 and H_2 pressure to closely control the rate of hydrolysis and hydrogenation step. For instance, a total pressure ($CO_2 + H_2$) of 40 bar and a CO_2/H_2 ratio of 3 was found to be optimal to produce HHD with 77 % yield from HMF. When the CO_2 pressure was kept constant at 30 bar while the hydrogen pressure was increased from 10 to 60 bar, the hydrogenation reaction became dominant and DHMF and 2,5-dihydroxymethyltetrahydrofuran (DHMTHF) were produced as the two main products. No production of HHD was observed in this case (entry 3). Similarly, when the CO_2/H_2 ratio

Table 1. Conversion of HMF to HHD in the dual acid/redox catalytic system.[a]



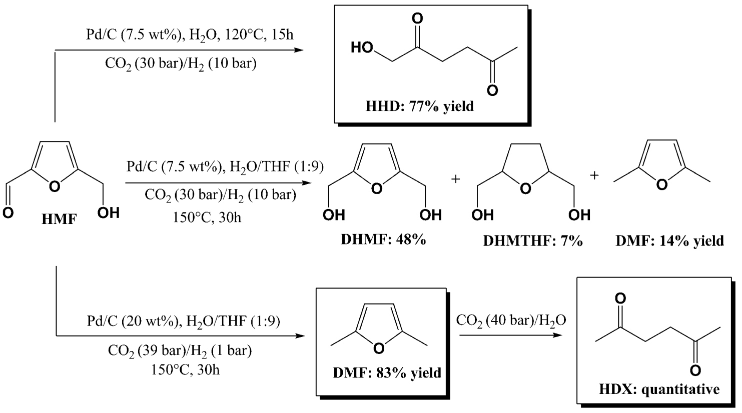
Entry	Pd/C [wt %]	P_{CO_2} [bar]	P_{H_2} [bar]	t [h]	Conv. [%]	Yield [%]	Select. [%]
1	7.5	30	10	15	100	77	77
2	7.5	35	5	15	81	54	67
3	7.5	30	60	15	95	0	0
4	7.5	10	30	15	90	33	37
5	3	30	10	15	46	20	43
6	14	30	10	15	100	62	62

[a] HMF (150 mg, 1.19 mmol), H_2O (5 mL).

was decreased from 3 to 0.33 while maintaining a total pressure of 40 bar, the yield of HHD dropped from 77 to 33 %, DHMF (28 % yield) and DHMTHF (7 % yield) were formed again as side products (entry 4). Preferentially, at a total pressure of 40 bar, the CO_2/H_2 ratio has to be maintained between 3 and 7. Note that although the selectivity of the reaction to HHD was not affected when the CO_2/H_2 ratio was raised to 7, this change however decreases the reaction rate. Indeed, at a CO_2/H_2 ratio of 7, only 81 % conversion of HMF was achieved after 15 h of reaction *vs* 100 % at a CO_2/H_2 ratio of 3 (entry 2). Evidently, the palladium content in the Pd/C catalyst influences the rate of the hydrogenation step and, thereby, the selectivity to HHD. A decrease of the amount of Pd/C from 7.5 wt % to 3 wt % not only slowed down the reaction but also decreased the selectivity to HHD due to dominant acid-catalyzed conversion of HMF to undesirable side products (entry 5). Reversely, an increase of the Pd content from 7.5 wt % to 14 wt % accelerated the formation rate of HHD but interestingly with no effect on the HHD selectivity (entry 6). However, a higher Pd/C loading than 14 wt % had a negative effect on the reaction selectivity and, in this case, hydrogenation reactions became dominant. Hence, in our conditions, the Pd/C loading should be maintained between 7.5 and 14 wt %.

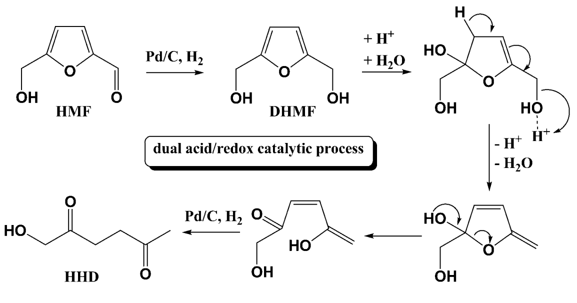
The nature of the solvent also plays a crucial role on the selectivity of the reaction. Interestingly, under similar conditions as those reported in Table 1, entry 1, the selectivity of the reaction was dramatically changed when working in a THF/H_2O mixture (9:1). Indeed, in this case (conv. = 91 %), DHMF (48 % yield) and DHMTHF (7 % yield) were produced together with DMF (14 % yield) while HHD was not detected (Scheme 4). Remarkably, when the pressures of CO_2 and H_2 were optimized, it was possible to drive the reaction towards DMF. For example, at a CO_2 and H_2 pressure of 39 bar and 1 bar, respectively, DMF was produced with 91 % selectivity at 57 % conversion (i.e., 48 % yield) after 30 h of reaction at 150 °C. One may suspect that a decrease of the amount of water led to the formation of less carbonic acid and thus the hydrogenolysis of HMF was favored, rationalizing the formation of DMF. Under these conditions, an increase of the Pd/C loading from 7.5 wt % to 20 wt % allowed the rate of hydrogenolysis reaction to be further increased and DMF was now produced with 83 % yield (Scheme 4). Notably, removal of CO_2 was detrimental for the production of DMF. Indeed, without CO_2 the reaction stopped at the DHMF and DHMTHF step, suggesting that acidity originating from the reaction between CO_2 and water may have a positive effect on the hydrogenolysis of DHMF to DMF, presumably by facilitating the dehydration step. Note that CO_2 may also facilitate the dissolution of hydrogen in the THF/H_2O system.[7]

Then, after removal of Pd/C and THF, DMF was quantitatively converted to HDX just by reaction under CO_2, as described in Scheme 2. One should comment that the possibility to drive our process to DMF just by changing the nature of the solvent is also of prime importance from an industrial point of view. Indeed, DMF has been recognized as a promising fuel additive because of its higher energy density as compared to ethanol (40 % greater), high octane number, and very low solubility in water. The flexibility of the process definitely reinforces its attractiveness for industrial implementation.[8]



Scheme 4. Tuning of the selectivity of the reaction as a function of the experimental conditions.

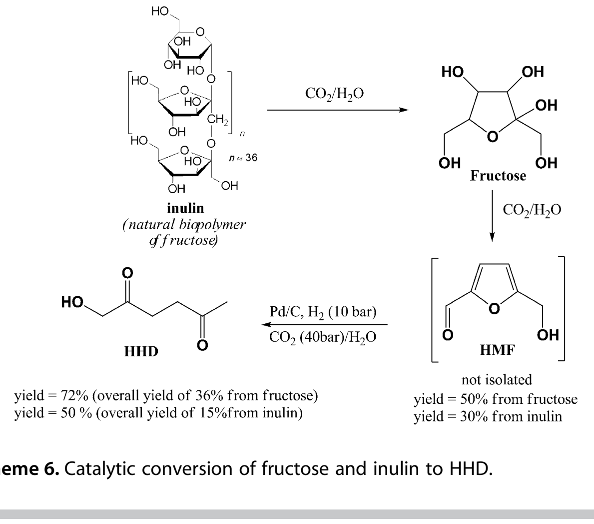
On the basis of literature reports and our experiments, a plausible reaction mechanism is provided in Scheme 5. Con-



Scheme 5. Plausible reaction mechanism.

sidering that HMF remained unaltered in the CO_2/H_2O system (without Pd/C and hydrogen), one may suspect that the first step is the hydrogenation of HMF to DHMF. Then, inspired by a previous mechanism reported for the production of levulinic acid from HMF,[9] the reaction mechanism may proceed here through (1) the acid-catalyzed rehydration of DHMF, followed by (2) a ring opening, and (3) a subsequent hydrogenation of the in situ-produced $C{=}C$ bond yielding HHD.

In a last set of experiments, we evaluated the direct conversion of fructose to HHD in a single reactor. To the best of our knowledge, production of HHD from fructose has not been reported before. Under our optimized conditions (7.5 wt% of Pd/C and a pressure of hydrogen and CO_2 of 10 bar and 30 bar, respectively), HHD was produced in a low yield (< 13%) although the conversion of fructose was complete. Hence, we investigated the direct conversion of fructose to HHD in a single reactor but in a sequential manner. Buxing Han et al. and our group have previously reported that the pK_a of carbonic acid is sufficient to catalyze the dehydration of fructose to HMF.[10] Keeping these results in mind, fructose was first heated in water at 150 °C under 40 bar of CO_2, resulting in the formation of HMF with a maximum yield of 50% (conv. fructose = 70%) after 10 h of reaction at 150 °C. Then, Pd/C (7.5 wt%), and H_2 (10 bar) were introduced into the reactor (the pressure of CO_2 and temperature were maintained at 40 bar and 150 °C, respectively) without intermediate purification of the aqueous phase containing HMF. In agreement with the results described above, HMF was converted into HHD in 72% yield (i.e., 36% yield from fructose; Scheme 6). In addition, the reaction also proceeded well starting from inulin, a natural biopolymer of fructose. In particular, after heating inulin in the CO_2/H_2O system at 150 °C and 40 bar, HMF was produced with 30% yield. Introduction of Pd/C (7.5 wt%) CO_2 (40 bar) and hydrogen (10 bar) into the reactor led to the production of HHD with 50% yield from HMF (i.e. 15% yield from inulin) after heating the reactor at 120 °C for 10 h (Scheme 6). In such case, the catalytic system was capable of promoting in a single reactor (1) the acid-catalyzed hydrolysis of inulin to fructose, followed by (2) the acid catalyzed dehydration of fructose to HMF, (3) the hydrogenation of HMF to DHMF, (4) the acid-catalyzed rehydration of DHMF, and finally (5) hydrogenation to HHD. Considering that five consecutive steps are necessary to convert inulin to HHD with 15% yield, one may deduce that the average yield corresponding to each elementary step is about 70% showing the rather selective efficiency of the process.



Scheme 6. Catalytic conversion of fructose and inulin to HHD.

We also focused on the use of glucose; a key raw material. Using an identical CO_2/H_2O system for converting fructose as aforementioned, no formation of HHD was observed. This result is in agreement with previous works, as production of furanic derivatives from glucose requires first an isomerization of glucose to fructose which cannot be catalyzed by carbonic acid. In such case, it was possible to produce HHD from glucose in a two-step process involving (1) conversion of glucose to HMF using our previously reported route (conversion of glucose to HMF with 70% yield in an aqueous phase containing a catalytic amount of $AlCl_3$),[11] followed by (2) the conversion of HMF to HHD. Using this two-step process, an overall yield of HHD of 50% was obtained from glucose. Note that all attempts to produce HHD from glucose by combining Pd/C, hydrogen, and $AlCl_3$ in a single reactor failed, mostly because pH required for the conversion of glucose to HMF and HMF to HHD are not compatible.

In summary, we show that Pd/C mediated hydrogenation of inulin, fructose, and HMF in water and under pressure of CO_2 opens a route to valuable diketone derivatives in a one-pot process. Under optimized conditions, five reaction steps consecutively and selectively take place in a single reactor, with an average yield of 70% for each step in the case of inulin. The reactions show a carbon economy of 100%, employ only water as a solvent, and require rather low hydrogen pressures (10 bar). On the other hand, the ability of CO_2 to produce carbonic acid in the presence of water not only facilitates the work-up procedure but also offers a solution to the deactivation of acid solid catalyst, often encountered in the presence of water. In addition, by changing the nature of the solvent, it is possible to switch the selectivity of the reaction either to DMF or HHD, which represents another noticeable advantage. We do believe that the concept of using CO_2 to generate acidity during hydrogenation reactions is of wide interest because it allows complexity and diversity to be created from carbohydrates, with a high eco-efficiency.

Experimental Section

Analytical methods: Gas chromatography analyses were performed on a Bruker GC-456 instrument equipped with an on-column injector (250 °C), an FID detector (325 °C) and an HP-5 ms column (30 m × 0.25 mm × 0.25 μm). NMR spectra were recorded on Bruker ADVANCE DPX 400 spectrometers at 400.13 MHz for ^1H and 100.6 MHz for ^{13}C. Data for HHD, DMF, HDX, HMF, LA, DHMF, and DHMTHF are already described in the existing literature, and were used to ascertain the formation of targeted products.

Selected data for HHD: ^1H NMR (400 MHz, $CDCl_3$): $\delta = 2.16$ (s, 3 H, $-CH_3$), 2.59 (t, $J = 6.4$ Hz, 2 H, $-CH_2$), 2.80 (t, $J = 6.4$ Hz, 2 H, $-CH_2$), 3.12 (bs, 1 H, $-OH$), 4.29 ppm (s, 2 H, $-CH_2$); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 29.7$ ($-CH_3$), 31.7 ($-CH_2$), 36.8 ($-CH_2$), 68.2 ($-CH_2OH$); LC/MS (ESI), $m/z = 132.1$ uma.

Procedure for the conversion of DMF to 2,5-hexanadione: DMF was dissolved in 5 g of water in a batch reactor. The mixture was heated under CO_2 (40 bar) for 15 h at 150 °C. At the end of the reaction the autoclave was cooled to room temperature and the pressure was released. The recovered aqueous solution was then analyzed by GC.

Procedure for the conversion of furfuryl alcohol to levulinic acid: Furfuryl alcool was dissolved in a mixture of 2-methyltetrahydrofuran/water (5 g:5 g) in a batch reactor. The mixture was heated under CO_2 (40 bar) for 15 h at 150 °C. At the end of the reaction, the autoclave was cooled to room temperature and the pressure was released, The recovered solution was then analyzed by GC.

Procedure for the hydrogenation of HMF to HHD: To a mixture of H_2O (5 mL) and HMF (150 mg, 1.19 mmol) was added Pd/C (11 mg, 0.0052 mmol). This solution was placed inside the autoclave and was flushed with H_2. Next, the autoclave was pressurized with H_2 to 10 bar and then CO_2 was added up to a total pressure of 40 bar. The reaction mixture was stirred and heated to 120 °C for 15 h. After this period, the autoclave was cooled to room temperature, vented, and opened. A syringe filter was used to remove the catalyst from the reaction mixture, and the recovered solution was then analyzed by GC.

Procedure for the hydrogenation of HMF to DMF: To a mixture of THF (5 mL), H_2O (0.5 mL) and HMF (150 mg, 1.19 mmol) was added Pd/C (20 wt %, 30 mg). This solution was then placed inside the autoclave and pressurized at 39 bar of CO_2 and 1 bar of H_2. The solution was then heated at 150 °C for 30 h. After this period, the reactor was cooled to room temperature, vented, and opened. A syringe filter was used to remove the catalyst from the reaction mixture, and the recovered solution was then analyzed by GC.

Procedure for the hydrogenation of fructose (or inulin) to hydroxy 2,5-hexanone: Fructose or inulin was dissolved in 5 g of water in a batch reactor. The mixture was heated under CO_2 (40 bar) for 10 h at 150 °C. At the end of the reaction the autoclave was cooled to room temperature and the pressure was released. Then to this solution was added Pd/C (4 mg, 0.0019 mmol). Next, the vessel was pressurized with H_2 (10 bar) and then CO_2 (30 bar). The reaction mixture was stirred and heated to 120 °C for 15 h. After this period, the vessel was cooled, vented, and opened. A syringe filter was used to remove the catalyst from the reaction mixture, and the recovered solution was then analyzed by GC.

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Keywords: biomass · carbon dioxide · diketones · heterogeneous catalysis · furanes

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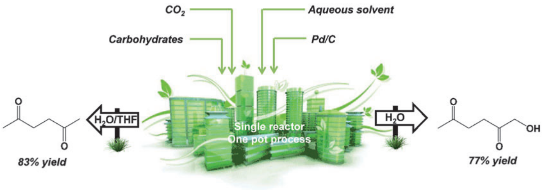
Palladium/Carbon Dioxide Cooperative Catalysis for the Production of Diketone Derivatives from Carbohydrates



Allez les verts! Valuable diketone derivatives are produced from carbohydrates and 5-hydroxymethylfurfural (HMF) through a flexible cooperative catalysis process involving a palladium/carbon dioxide system. Key to the process is reversible in situ formation of carbonic acid, which is capable of assisting Pd/C during the hydrogenation reaction by promoting the dehydration of carbohydrates and the ring-opening of furanic intermediates.